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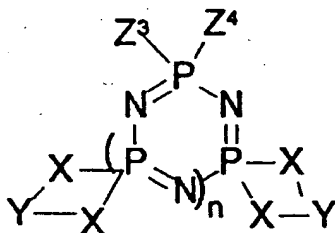
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(54) Flame-retarded epoxy systems; spirocyclic phosphazenes

(57) Curable compositions comprise at least one spirocyclic phosphazene having at least two epoxy curing functionalities and one or more epoxy resins. Cured resins and composites are formed with flame-retardant properties.

Some of the spirocyclic phosphazenes are claimed, namely those having a nucleus of the general Formula



where n is an integer, preferably 1 or 2;

each X independently represents O, S, or NR where R is H or alkyl of up to 5 carbon atoms, or aryl of up to 10 carbon atoms; each Y independently represents the atoms selected from C, N, O, S required to complete a stable cyclic structure; and Z³ and Z⁴ are independently selected from NHR¹ and -XR² where R¹ is H or aryl and R² is an alkyl or aryl group substituted with an epoxy curing functionality and X has the same meaning as before.

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FLAME RETARDED EPOXY SYSTEMS

This invention relates to epoxy resins and composites, particularly to spirocyclic phosphazene curatives for epoxy resins, to produce cured resins and composites having high Tg values and good flame retardant properties. These resins and composites are useful for example as structural and furnishing materials in transport, particularly aerospace applications.

There are increasing opportunities for non halogen materials with improved fire, smoke and toxicity properties in a range of market areas including aerospace, other transportation and electrical applications. This is being driven by increased customer demands and more stringent fire specifications. As materials are demonstrated with improved properties, this will result in further tightening of regulations.

Additionally, for structural and furnishing applications there is a requirement for light, stiff, strong, tough materials. Epoxy materials have been proposed for this application, but exhibit poor flammability properties.

Furnishing applications in aircraft (wall and ceiling panels, overhead baggage bins etc.) are subject to particularly stringent flammability test protocols and are currently met on a cost effectiveness basis by utilising phenolic resins. However, such resins, although excellent in terms of flammability, are poor in other important respects such as ease of handling, and therefore cost, and also in adhesion to other composite interior panel components e.g., the fibre reinforcement and lightweight aramid honeycomb. An objective for epoxy systems is to match the flammability performance of the phenolic systems, and to improve on their poor ease of handling and adhesion aspects etc. If a high glass transition temperature (Tg) characteristic can be built into such systems then structural applications, including flooring panels etc. may also be envisaged.

A detailed description of the general technology of epoxy resins and curatives, and the application of these materials in composites with fibrous reinforcing agents, including methods of fabrication, may be found in the following publications (and references therein): 'Encyclopedia of Polymer Science and Engineering', H.H. Mark and J.I. Kroschwitz, eds., Wiley Interscience publ., Vol. 3, pp 776-820 (composites), and Vol. 6 pp 322-382 (1986) (epoxy resins), and more recently in 'Kirk-Othmer Encyclopedia of Chemical Technology', 4th ed., J.I. Kroschwitz and M. Howe-Grant, eds., Wiley Interscience publ., Vol. 7, pp 1-77 (1993) (composites) and Vol. 9, pp 730-755 (1994) (epoxy resins).

Halogenated flame retardants have been used with epoxy resins, but these give rise to high emissions of smoke and toxic/corrosive gases, and are therefore unacceptable for the applications detailed above.

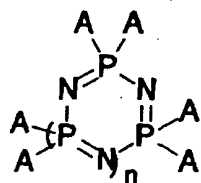
Non halogen flame retardants are preferred, and may be divided into two classes: additive and reactive. Additive flame retardants do not participate in the epoxy resin curing reaction, but are merely present as a diluent. Hence there is often a deterioration in physical and/or mechanical properties associated with their use. Also, there is potential for the additive to migrate to the surface and/or to be leached out under certain conditions of storage or use.

Elemental red phosphorus is an example of a non halogen additive flame retardant, and typically 5-10% by weight would be used in an epoxy system, as described for example in 'Handbook of Flame Retardant Chemicals and Fire Testing Services', Technomic Publishing Co. (1988), pp 40-42.

Curative flame retardants participate in the curing process and hence become chemically bonded to the cured epoxy resin. There is still some reduction in performance compared to unmodified epoxy formulations which restricts the utility of these

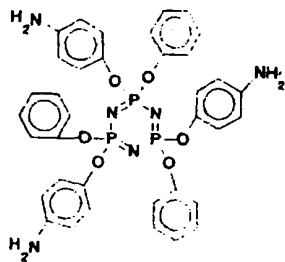
compositions.

Phosphazenes, especially cyclic phosphazenes such as cyclotriphosphazenes have found widespread use both as additive and as curative flame retardants. Cyclic phosphazenes possess a ring consisting of alternating phosphorus and nitrogen atoms, as shown in the following formula:

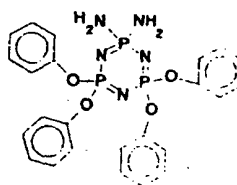


in which n is an integer (normally 1) and each A represents an organic group. Typical identities of A include amino, allylamino, arylamino, alkoxy, aryloxy and alkylthio.

Compounds of formula (1) in which two or more A groups are primary or secondary amino groups are capable of acting as curing agents for epoxy resins. Examples are disclosed e.g., in D. Kumar et al, J. Polymer Sci., Poly. Chem. Ed., Vol. 22, pp 927-943, (1984), and US 4,745,206. Known compounds of this type include the following:



COMPOUND A



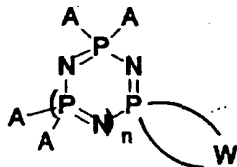
COMPOUND B

The use of these two compounds to cure epoxy resins is described in US 4,668,589, and D. Kumar, J. Polym. Mater., Vol. 7, pp 215-220, (1990), (Compound A), and K. Takahashi et al, Kobunshi Ronbunshu, Vol. 47, pp 757-762 (1990), (Compound B).

These phosphazene curatives are normally used without co-curatives. In typical formulations of Compound A described in US 4,668,589, the resulting level of incorporation of phosphorus is 5-7% by weight.

A limitation of these materials is the relative complexity of the synthesis. Taking Compound A as a typical example, its preparation from hexachlorocyclotriphosphazene is described in J. Polymer Sci., Poly. Chem. Ed., Vol. 22, pp 927-943, (1984). This synthetic procedure takes at least a week to complete, and results in a mixture of four compounds. Additionally, the T_g values obtained with such cured compounds are reduced over other cured epoxy resin systems.

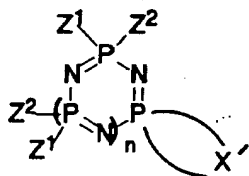
A separate class of cyclic phosphazenes are the spirocyclic phosphazenes, in which at least one P atom of the cyclophosphazene system additionally forms part of another ring, as shown in the following formula:



in which A has the same meaning as before, n is an integer (normally 1 or 2), and W represents the atoms (usually selected from C, N, O and S) required to complete a cyclic system including the P atom. A few examples of this class of compound are described in US 3,294,872, US 3,356,769, and R.A. Pelc et al., Phosphorus, Sulfur and Silicon, Vol. 47, pp 375-382, (1990).

A number of compounds of this type have been disclosed which incorporate primary or secondary amine functionalities in Allcock and Kugel, Inorg. Chem., Vol 5, pp 1016-1020 (1966), US 3,299,128, DE 2 313 531, W.F. Deutsch and R.A. Shaw, Phosphorus, Sulfur and Silicon, Vol. 47, pp 119-140 (1990).

This invention relates to flame retarded high Tg cured epoxy resins, and composite materials prepared from them. In a first aspect of the invention there is provided a curable composition comprising at least one spirocyclic phosphazene having at least two epoxy curing functionalities and one or more epoxy resins. In preferred embodiments, the spirocyclic phosphazene has the formula:-



wherein Z^1 and Z^2 are organic groups or comprise the atoms selected from C, N, O and S required to complete a cyclic structure and

X' represents the atoms selected from C, N, O, S to complete a stable cyclic structure, wherein at least 2 epoxy curing functionalities are present in the molecule either as substituents on one or more of the moieties defined by X' , Z^1 and Z^2 or as integral parts of those moieties.

The incorporation of these spirocyclic phosphazene flame retardant curatives does not substantially reduce the Tg of the epoxy system, when compared to an analogous formulation with a typical amine curative for epoxy resins.

The resulting cured systems exhibit excellent flammability performance, with low levels of emission of smoke and toxic gases. Since it is possible to prepare cured formulations which do not contain appreciable levels of halogens, there is no risk of the emission of toxic and corrosive halogen acid gases (HCl or HBr) in a fire.

The compositions may also include other curing agents, toughening resins and fibres.

Such cured resin systems or composites containing these resins

may be used in many known applications of epoxy resin/composite systems. These applications include structural and furnishing materials for use in transport, particularly aerospace markets. Additional applications include automotive, railways, building construction and electronics.

Some spirocyclic phosphazene compounds have been suggested to have utility as additive flame retardants in various host polymer systems, as disclosed in some of the references already mentioned (e.g., as treatments for fabrics). However there is no reference to the use of this class of compound as a flame retardant curative for epoxy resins.

The curatives of this invention have been found to be particularly effective flame retardants in toughened epoxy systems, giving optimum fire properties at unexpectedly low incorporation levels. They are normally used with non phosphazene co curatives, with typically only 5-20% of the total molar amount of curative functionality being provided by the spirocyclic phosphazene curative. This corresponds to around 0.5 to 2% by weight incorporation of phosphorus into the formulation, compared to typically 5-10% for prior art additive and curative phosphorus flame retardants.

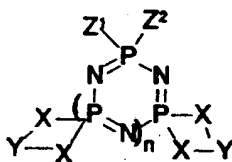
The resulting zero halogen cured materials show significant benefits in terms of reduced smoke and toxic gas emission during fire, and good thermomechanical properties (high wet Tg). When compared with a typical prior art non spirocyclic phosphazene curative (Compound A) in similar cured epoxy formulations, a higher Tg is obtained with a spirocyclic phosphazene curative of this invention.

Spirocyclic phosphazene curing agents suitable for use in the invention are cyclic phosphazenes in which at least one of the phosphorus atoms forms part of a ring that is distinct from the phosphazene ring. Preferably at least two of the phosphorus

atoms form part of spiro-linked rings.

In addition, the spirocyclic phosphazenes suitable for use in the invention possess at least two groups capable of participating in the curing of epoxy resins. Such groups are well known in the art of epoxy resin curing, and include amino groups (primary or secondary), amide groups, phenol groups, carboxylic acid groups, etc. Amino groups, especially primary amino groups, are preferred. Preferably, in order to impart low emissions of smoke and toxic gases, the curing agent should not contain appreciable levels of halogen. However, halogenated examples of such materials would also be expected to be effective both as flame retardants and curing agents.

Preferred spirocyclic phosphazene curing agents for use in the invention have a nucleus of formula (3):



in which:

n is an integer (preferably 1 or 2);

each X independently represents O , S , or NR where R is H , or alkyl of up to 5 carbon atoms, or aryl of up to 10 carbon atoms;

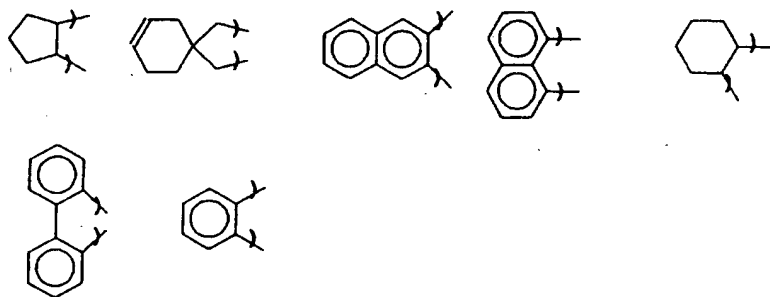
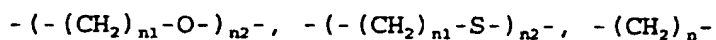
each Y independently represents the atoms, selected from C , N , O , S , required to complete a stable cyclic structure;

Z^1 and Z^2 independently represent organic groups, or Z^1 and Z^2 together represent the atoms, selected from C , N , O , S , required to complete a stable cyclic structure;

and at least 2 epoxy-curing functionalities are present in the molecule, either as substituents on one or more of the moieties defined by X , Y , Z^1 and Z^2 , or as integral parts of these moieties.

Preferably $X = O$ or NH . Embodiments in which $X = NH$ exemplify the situation in which epoxy-curing functionalities are an integral part of a ring defined by X and Y .

Examples of moieties defined by Y include:

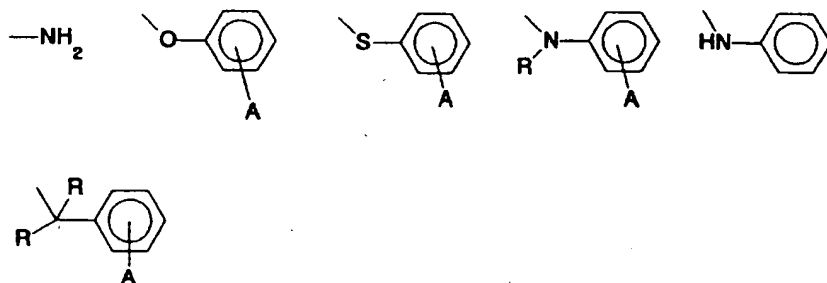


In these examples, $'-)-'$ indicates the points of attachment to the X groups. Additional substituents may also be present on these linking structures, particularly on the aromatic ring structures.

Moieties defined by Z^1 and Z^2 preferably satisfy the formula R^3-X where X has the same meaning as before, and R^3 is H or an alkyl or aryl group substituted with an epoxy-curing functionality.

Alternatively, Z^1 and Z^2 together may be represented by the formula $-X-Y-X-$, where X and Y have the same meanings as before.

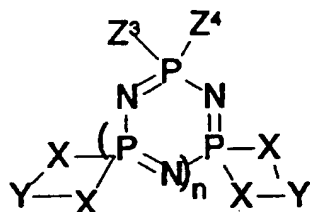
Specific examples of moieties represented by Z^1 and Z^2 include:



where A = H, NH₂, NHR, OH or SH; and R = H, alkyl or aryl

Preferred spirocyclic phosphazene curing agents for use in the invention include Compounds I - VII, as described in the Experimental Examples below.

In a separate aspect of the invention, certain spirocyclic phosphazene curing agents are claimed as novel compositions of matter. In accordance with this aspect, there is provided a spirocyclic phosphazene having a nucleus in accordance with the formula:



where:

n is an integer, preferably 1 or 2;

X and Y have the same meanings as before; and

Z³ and Z⁴ are independently selected from -NHR¹ and -XR²,

where R¹ is H or aryl,

R² is an alkyl or aryl group substituted with an epoxy-curing functionality, and X has the same meaning as before.

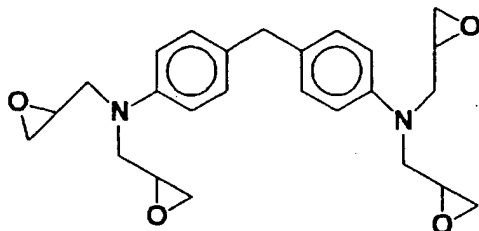
Examples of this class which do not contain appreciable levels of halogens are preferred, but it is expected that compounds with halogenated substituents, particularly -Br and -Cl, will also be effective as both flame retardants and curatives.

The synthesis of the examples demonstrated below of novel spirocyclic materials is relatively simple comprising two reaction steps from hexachlorocyclotriphosphazene, and results

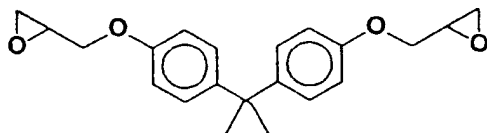
in high purity products in good yield. This represents a significant advantage in ease of preparation compared to typical prior art phosphazene curatives.

Examples of these novel spirocyclic phosphazene curing agents may be prepared for example by the reaction of an aminophenoxide with 1,1,3,3,-bisspiro(2,2'-dioxybiphenyl)-5,5-dichlorocyclo-triphosphazene. The latter may be prepared for example as described in R.A. Pelc et al., Phosphorus, Sulfur and Silicon, Vol. 47, pp 375-382, (1990).

Epoxy resins which are particularly useful in this invention include TGDDM (N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenylmethane) epoxy resin, e.g., Araldite MY720 and MY9512 from Ciba:



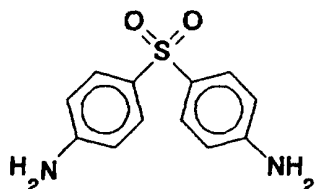
and DGEBA (diglycidyl ether of bisphenol A) epoxy resin, e.g., Epikote 828 from Shell:



A particularly preferred epoxy resin system is a 1:1 mixture by weight of TGDDM and DGEBA epoxy resins.

Co-curing agents for epoxy resins include aliphatic and aromatic amines (primary and secondary), anhydrides, organic acids,

imidazoles, mercaptans and hydroxy compounds. Aromatic amines are preferred for use as co-curatives with the phosphazenes of this invention. A particularly preferred co-curative is DADS (4,4'-diaminodiphenylsulphone), e.g., HT976 from Ciba:



The ratio of phosphazene to co-curatives will affect the viscosity of the uncured epoxy/curative mixture and also the flammability properties of the cured resin system. In general the preferred range of ratio of phosphazene to co-curatives is chosen to give a ratio of moles of curative functionality between 1:99 and 50:50 moles arising from phosphazene and co-curatives respectively, with a most preferred range of molar ratio of 5:95 to 20:80. This range is surprisingly low compared to prior art phosphazene curatives, which are typically used without co-curatives.

Thermoplastic toughening agents may be added to the epoxy/curative formulations of this invention in order to reduce brittleness of the cured resin systems. Suitable thermoplastic materials should have high thermal stability, for example polyether sulphones, polyetherimides e.g., Ultem 1000 polyetherimide from G.E. Plastics. Typically, 5-10% by weight of thermoplastic toughening agent is added.

Incorporation of such thermoplastic toughening agents may be achieved by dissolving the thermoplastic and epoxy resin in a suitable solvent (e.g., dichloromethane), and then removing the solvent to form a semi-solid thermoplastic/epoxy combination. This thermoplastic/epoxy combination is then added to a further quantity of epoxy resin and curatives and stirred/heated until a homogeneous mixture is obtained. The curative may be

introduced as a fine powder if its melting point is high, and may remain as a powder when it is initially incorporated. The ratio of curative to epoxy resin is normally calculated so that a stoichiometric quantity of curative is present. Thus a total of one mole of curative groups is present per mole of epoxy groups. In some cases other ratios may be used e.g., an excess of curative.

Other additives which are suitable for incorporation into curable epoxy formulations may also be present e.g., pigments, antioxidants, accelerators etc.

The overall mixture of epoxy/curatives/toughener is then poured into a mould and heated further until the curatives have melted and curing occurs. For the preferred compositions of this invention, a cure schedule of two hours at 180°C followed by two hours at 210°C was found to be appropriate.

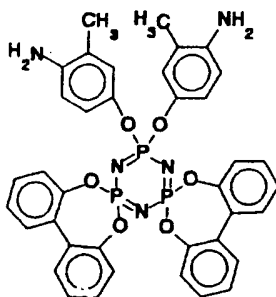
These materials are designed for incorporation into composites, particularly carbon fibre composites, to produce strong, stiff, lightweight materials with a combination of excellent flammability and thermomechanical properties. These composites have application as structural and furnishing components, particularly in applications where low weight is important e.g., aerospace and other transport areas.

Composite laminates may be prepared from such formulations by coating layers of reinforcing materials e.g., fibres with uncured epoxy/ curative/toughener system to form a 'prepreg' of typically one part resin and two parts fibres by weight, and then assembling these layers of prepregs to form a composite laminate, which is then cured e.g., under pressure in an autoclave. Lightweight structures may be achieved by incorporating honeycomb cores of e.g., polyimides between surface layers of prepregs. Suitable materials for use as reinforcements include carbon and glass fibres.

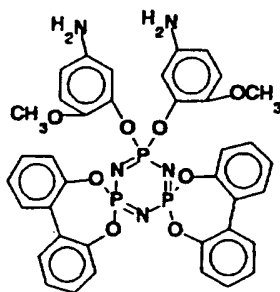
For one material (Compound I) extensive flammability characterisation in untoughened and toughened epoxy systems has been performed.

The chemical structure shows a macrocyclic ligand with two phosphorus atoms (P) and two amine groups (H₂N). The ligand is composed of two 1,3-phenylene groups (benzene rings with a meta-substitution pattern) and two 1,3-phenylene groups (benzene rings with a meta-substitution pattern). The phosphorus atoms are connected by a central bond, and each phosphorus atom is also bonded to an oxygen atom (O) and a nitrogen atom (N). The nitrogen atoms are part of the 1,3-phenylene groups. The amine groups are attached to the 1,3-phenylene groups via oxygen atoms (O).

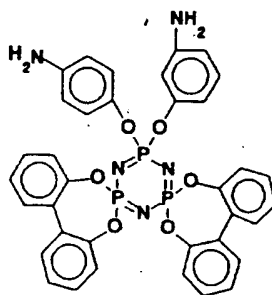
Compound III



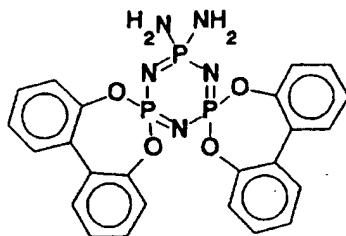
Compound IV



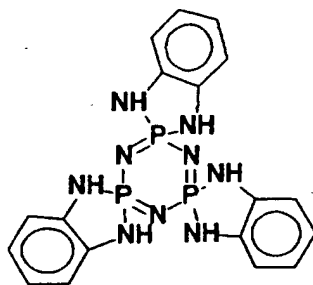
Compound V



Compound VI



Compound VII



The following materials were used in the experimental examples described below:

Epoxy resins:

TGDDM epoxy resins: Araldite MY720 and MY9512 from Ciba
(epoxy equivalent weight = 125 g)

DGEBA epoxy resin: Epikote 828 from Shell
(epoxy equivalent weight = 187 g)

Curatives:

DADS (4,4'-diaminodiphenylsulphone): HT976 from Ciba
(curative equivalent weight = 62 g)

(All other curatives were prepared as described in the experimental examples.)

Thermoplastic toughening agent: Ultem 1000 polyetherimide from G.E. Plastics

Curatives (total) were used at 100% of the stoichiometric level. Thus a total of one mole equivalent of curative groups is present per mole equivalent of epoxide groups. The weight percent of each material required in the formulation examples may be calculated from the epoxy and curative equivalent weights of each material. The epoxy (or curative) equivalent weight is the weight in grammes of epoxy resin (or curative) which contains one mole equivalent of epoxide (or curative) groups, i.e., the molecular weight in grammes divided by the number of epoxide (or curative) groups present in each molecule. In the case of amine curatives, the number of curative groups is equal to the number of active hydrogens.

The following method was used for mixing and curing of epoxy formulations:

For toughened formulations, the thermoplastic toughening agent is first mixed with the epoxy resins in batches from which material to be cured is removed. Typically, the thermoplastic toughening agent is dissolved in dichloromethane (DCM) in a glass jar with agitation. Once dissolved, the two epoxy resins Araldite MY 9512 and Epikote 828 are added in a 2:1 w/w ratio and mixing continued (further Epikote 828 is added subsequently to give a 1:1 ratio). All mixing was generally carried out in conventional laboratory glassware. Stirring was accomplished using an air motor driving a normal paddle stirrer.

When a homogeneous mixture has been obtained, as much DCM as possible is removed using a rotary evaporator at 80°C. The mixture is then heated in a vacuum oven at 50°C until frothing ceases. The temperature is then raised to 120°C for 2-3 hours to complete the removal of solvent and form a thermoplastic polymer mixture.

Additional amounts as required of the two epoxy resins to give a 1:1 ratio are first mixed together at 80°C. The DADS curative is then dissolved in the epoxy mixture, with stirring, at 120°C. The addition is typically accomplished over 20 minutes. The thermoplastic polymer mixture is then added in pieces and stirring continued until dissolved.

The epoxy curative mixture is then cooled to 100°C and crystalline spirocyclic phosphazene curative e.g., Compound I (particle size < 100 microns) added over 20 minutes. The crystalline Compound I does not dissolve appreciably at this temperature. The resulting liquid is then degassed under reduced pressure (1 mbar) for 45 minutes at 100°C to remove air bubbles. The resulting mixture is then briefly heated to 130°C to reduce viscosity and transferred to a pre-heated, release coated, aluminium/PTFE mould and cured under the following cure schedule: 130°C ramped to 180°C at 2°C per minute and maintained for 2 hours before being ramped to 210°C at the same rate and maintained for a further 2 hours.

The above mixing procedure was chosen as being suitable for small scale laboratory work. Other methods may be suitable for larger scale mixing of these types of formulations for example as described in the general references on epoxy resins cited above.

The following evaluation methods were used to determine properties of uncured and cured epoxy systems:

Thermal analysis:-

- TGA 20°C/min 30-580°C under air or N₂
- DSC 10°C/min 30-280°C under N₂
- DMA generally in 3 point bending mode, 5°C/min 30-280°C under He, 1Hz frequency
modulus loss E' - tangential method, not tan delta
(except where indicated).

Humidity ageing - 71°C for two weeks, 100% RH or 2 days in boiling water

Flammability:-

- LOI (limiting oxygen index) as per ASTM D 2863

- Cone calorimetry as per ASTM E 1354 (horizontal orientation) and employing a grid to restrain intumescence. The heat flux for cone calorimetry experiments was 50 kW/m² in all cases.

Sample size was 3x100x100 mm.

Example 1:-

Preparation of 1,1,3,3-bisspiro(2,2'-dioxybiphenyl)-5,5-bis(3-aminophenoxy)cyclotriphosphazene (Compound I)

Sodium hydride (7.5g, 80% NaH in oil, 0.25 mol) was added slowly to a stirred solution of 3-aminophenol (27.2g, 0.25 mol) in dry tetrahydrofuran (500ml) contained in a 2-litre round bottomed flask equipped with a stirrer, nitrogen supply, thermometer and condenser. The mixture was stirred at room temperature for 30 minutes and was then heated at reflux for three hours under nitrogen. The mixture was allowed to cool and 1,1,3,3-bisspiro(2,2'-dioxybiphenyl)-5,5-dichlorocyclotriphosphazene, (57.4g, 0.1 mol) was added. The latter material is hereafter designated Compound VIII, and was prepared as described in R.A. Pelc et al., Phosphorus, Sulfur and Silicon, Vol. 47, pp 375-382, (1990).

The reaction was then heated at reflux for 19 hours under nitrogen and the mixture filtered through a pad of celite. The filtrate was poured slowly into a beaker containing rapidly stirred petroleum spirit (bp 60-80°C, 2.5 litres). The resulting colourless solid was filtered off, washed with a little petroleum spirit (bp 60-80°C, 50ml) and dried in vacuo over phosphorus pentoxide. The isolated solid was identified as 1,1,3,3-bisspiro(2,2'-dioxybiphenyl)-5,5-bis(3-amino-phenoxy)cyclotriphosphazene.

Yield: 62g, 86%, melting point 263°C (by DSC).

The isolation method described for Compound I above (involving an approximate 5.5:1 ratio of non-solvent to solvent) resulted in a crystalline sharp melting solid. By increasing the ratio to about 11:1 an amorphous solid was isolated. DSC data for the crystalline material revealed a sharp melting transition at 263°C whilst the substantially amorphous material revealed a T_g at 100°C, a crystallisation at 196°C followed by a melt at 263°C. A stoichiometric quantity of the amorphous material dissolved in an epoxy, e.g., Epikote 828, at 130°C to give a transparent viscous liquid. A stoichiometric quantity of the crystalline material (jet-milled to < 53 micron particle size) remained undissolved and did not totally dissolve until 170°C (hot-stage microscope observation) i.e., it did not dissolve until the cure onset temperature.

Example 2:

Preparation of 1,1,3,3-bispiro(2,2'-dioxybiphenyl)-5,5-bis(4-aminophenoxy)cyclotriphosphazene (Compound II)

Sodium hydride (7.5g, 80% NaH in oil, 0.25 mol) was added slowly to a stirred mixture of 4-aminophenol (27.2g, 0.25 mol) in dry tetrahydrofuran (500 ml) contained in a 2-litre round bottomed flask equipped with a stirrer, nitrogen supply, thermometer and condenser. The mixture was stirred at room temperature for 30 minutes and was then heated at reflux for 20 hours. The mixture was allowed to cool and Compound VIII (57.4g, 0.1 mol) and dry tetrahydrofuran (100 ml) added. The reaction was then heated at reflux for 26 hours under nitrogen and the mixture filtered through a pad of celite. The filtrate was poured slowly into a beaker containing rapidly stirred petroleum spirit (bp 60-80°C, 3 litres). The resulting grey solid was filtered off, washed with a little petroleum spirit (bp 60-80°C, 50ml) and dried in vacuo over phosphorus pentoxide. The isolated solid was identified as 1,1,3,3-bispiro (2,2'-dioxybiphenyl)-5,5-bis(4-aminophenoxy)cyclotriphosphazene.

Yield: 65.6g, 90%, DSC: mp. 299°C

Example 3:

Preparation of 1,1,3,3-bisspiro(2,2'-dioxybiphenyl)-5,5-bis(4-amino-3-methylphenoxy)cyclotriphosphazene (Compound III)

Sodium hydride (0.75g, 80% NaH in oil, 0.025 mol) was added slowly to a stirred solution of 4-amino-3-methylphenol (3.08g, 0.025 mol) in dry tetrahydrofuran (50ml) contained in a 250 ml 3-necked round bottomed flask equipped with a stirrer, nitrogen supply, thermometer and condenser. The mixture was stirred at room temperature for 30 minutes and was then heated at reflux for one hour under nitrogen. The mixture was allowed to cool and Compound VIII (5.74g, 0.01 mol) added. The reaction was then heated at reflux for 29 hours under nitrogen and the mixture filtered through a pad of celite. The filtrate was poured slowly into a beaker containing rapidly stirred petroleum spirit (bp 60-80°C, 500ml). The resulting grey/purple solid was filtered off, washed with a little petroleum spirit (bp 60-80°C, 20ml) and dried in vacuo over phosphorus pentoxide. The isolated solid was identified as 1,1,3,3-bisspiro(2,2'-dioxybiphenyl)-5,5-bis-(4-amino-3-methylphenoxy)cyclotriphosphazene.

Yield: 4.92g, 66%, DSC: mp. 252°C

Example 4:

Preparation of 1,1,3,3-bisspiro(2,2'-dioxybiphenyl)-5,5-bis(5-amino-1-methoxyphenoxy)cyclotriphosphazene (Compound IV)

Sodium hydride (0.75g, 80% NaH in oil, 0.025 mol) was added slowly to a stirred solution of 5-amino-1-methoxyphenol (3.48g, 0.025 mol) in dry tetrahydrofuran (80ml) contained in a 250 ml 3-necked round bottomed flask equipped with a stirrer, nitrogen supply, thermometer and condenser. The mixture was stirred at room temperature for 1 hour and was then heated at reflux for a further hour under nitrogen. The mixture was allowed to cool and Compound VIII (5.74g, 0.01 mol) added with dry tetrahydrofuran (50 ml).

The reaction was then heated at reflux for 24 hours under nitrogen and the mixture filtered through a pad of celite. The filtrate was poured slowly into a beaker containing rapidly stirred petroleum spirit (bp 60-80°C, 700ml). The resulting grey/purple solid was filtered off, washed with a little petroleum spirit (bp 60-80°C, 20ml) and dried in vacuo over phosphorus pentoxide. The isolated solid was identified as 1,1,3,3-bisspiro(2,2'-dioxybiphenyl)-5,5-bis(5-amino-1-methoxyphenoxy)cyclotriphosphazene.

Yield: 7.51g, 96%, DSC: no melt observed

Example 5:

Preparation of 1,1,3,3-bisspiro(2,2'-dioxybiphenyl)-5-(3-aminophenoxy)-5-(4-aminophenoxy)cyclotriphosphazene (Compound V)

Sodium hydride (80% NaH in oil, 0.3g, 0.01 mol) was added slowly to a stirred mixture of 4-aminophenol (1.09g, 0.01 mol) in dry tetrahydrofuran (60ml) contained in a 250 ml three-necked round bottomed flask equipped with a stirrer, nitrogen supply, thermometer and condenser. The mixture was stirred at room temperature for 1 hour and then heated at reflux for a further twenty hours under nitrogen. The mixture was allowed to cool for later use.

Sodium hydride (80% NaH in oil, 0.3g, 0.01 mol) was added slowly to a stirred solution of 3-aminophenol (1.09g, 0.01 mol) in dry tetrahydrofuran (60 ml). The mixture was stirred at room temperature for 40 minutes and then heated at reflux for 4 hours, the mixture was then cooled to room temperature and placed in an ice/salt/water bath. The internal temperature was reduced to <10°C and Compound VIII (5.74g, 0.01 mol) added.

The mixture was stirred at <10°C for 4 hours under nitrogen. TLC indicated the absence of starting material. The sodium 4-

aminophenoxide slurry was added to the reaction mixture and the mixture heated at reflux for 24 hours. The mixture was then filtered through a pad of celite and the filtrate poured slowly into a beaker containing rapidly stirred petroleum spirit (bp 60-80°C, 1 litre). The resulting pale grey solid was filtered off, washed with a little petroleum spirit (bp 60-80°C, 20ml) and dried in vacuo over phosphorus pentoxide. The isolated solid was identified as 1,1,3,3-bispiro(2,2'-dioxibiphenyl)-5-(3-aminophenoxy)-5-(4-aminophenoxy)cyclotriphosphazene containing approx. 17% (by NMR) of Compound I.

Yield: 6.22g, 86%, DSC: no melt observed

Example 6:

Preparation of 1,1,3,3-bispiro(2,2'-dioxibiphenyl)-5,5-diamino-cyclotriphosphazene (Compound VI)

Compound VIII (1.0g, 0.00174 mol), tetrahydrofuran (100 ml) and ammonia solution (S.G. 0.88, 1.5g) were combined in a 250ml flask and heated at reflux for 18 hours. The reaction mixture was hot-filtered and the filtrate evaporated to dryness. 1,1,3,3-bispiro(2,2'-dioxibiphenyl)-5,5-diaminocyclotriphosphazene was isolated as a colourless solid.

Yield: 0.81g, 87%, DSC: mp. 320°C

Example 7:

Compounds I-V as Curatives Conferring High Tg Characteristics in an Epoxy System

Amorphous samples of Compounds I-V were (hot melt) dissolved in a stoichiometric amount of an epoxy resin [Epikote 828] at 120°C to give a transparent yellow-brown viscous liquid. A further example is included in which Compound I was co-dissolved in tetrahydrofuran with a stoichiometric ratio of Epikote 828. After drying in air for 5 hrs (<0.5% solvent left by TGA) the

product was a transparent pale yellow sticky viscous liquid.

Two further comparative examples are included - one utilising diaminodiphenylsulphone (DADS), and the other 1,3,5-triphenox-1,3,5-tris-(4-aminophenoxy)cyclotriphosphazene (Compound A). DADS is a widely used commercially available curative for high Tg epoxy systems, and Compound A is a known phosphazene epoxy curative, as described for example in US 4, 668, 589. Compound A was prepared by the addition of 3 equivalents of sodium phenoxide to compound VIII in tetrahydrofuran, followed by the addition of 3 equivalents of sodium 4-aminophenoxide.

In a typical experiment ca. 1g of resin/curative formulation was made - more than sufficient for the DSC studies below.

DSC Data on Curative/Epikote 828 System at 100% of Stoichiometry

Curative	Curative Equiv. Wt./g	Peak Exotherm	Onset/ °C	Magnitude J/g	Tg/°C
Examples of this invention					
Compound I	180	205	148	112	178
Compound I*	180	209	172	143	179
Compound II	180	221	132	-	175
Compound III	187	193	136	-	165
Compound IV	195	171	128	50	176
Compound V	180	193	148	122	175
Comparative examples					
DADS	62	220	168	194	193
Compound A	123	174	126	64	128

* Solvent mixed system, all the rest are hot melt

It is surprising that the Tg values for the spirocyclic amino phosphazene systems (i.e., those containing Compounds I-V) are very much higher than that for the system containing the comparative phosphazene Compound A, when compared directly in the same epoxy system. The high Tg values noted for Compounds I, II,

IV and V are similar to that obtained for DADS. The latter is widely used as a curative in current high Tg epoxy resin systems. Comparison of the magnitudes of the exotherms in the hot melt and solution mixed systems for Compound I suggests that a degree of cure advancement is taking place in the hot melt case. The Tg values are practically the same however. The magnitudes of the exotherms for Compounds I, IV and V are much less than for DADS, suggesting the cross-link density is less.

Example 8:

Thermal and Thermomechanical Properties of Cured Epoxy Systems Containing Spirocyclic Phosphazene Curatives

The epoxy resin system chosen for this study was Epikote 828/Araldite MY 720 (1:1 by weight). In all cases a stoichiometric quantity of amine curative was employed - either as one component or as equal molar quantities of two components. In general the epoxies were mixed at 80°C. In formulations where DADS was employed as a co-curative it was added first and dissolved at 120-130°C. After DADS dissolution Compound I or II (in amorphous form) was added and dissolved at the same temperature. The samples thus produced were cured at 180°C for 2 hrs. and 210°C for a further 2 hrs. A further example is included in which Compound I was co-dissolved in tetrahydrofuran with a stoichiometric ratio of the Epikote 828/MY 720 epoxy mixture. The mixture was coated onto woven glass fibre, dried at 60°C for 30 mins. and cured as above.

As an example of a nitrogen-linked spirocyclic phosphazene curative, Compound VII (structure shown above) was prepared according to the method of Allcock and Kugel, Inorg. Chem., Vol. 5, pp 1016-1020 (1966) by the reaction of three equivalents of 1,2-phenylene diamine with hexachlorocyclotriphosphazene in the presence of triethylamine in dry tetrahydrofuran. Chemical analysis and NMR spectra were consistent with the required

product.

A cured epoxy system containing Compound VII was also prepared according to the method above. The formulation used was 50% stoichiometry of Compound VII and 50 % DADS in 1:1 Epikote 828/Araldite MY 720 (1:1 by weight). The curative equivalent weight of Compound VII is 76 g. DSC of the uncured mixture shows a broad exotherm with onset at 150°C.

The dry and wet (samples conditioned 2 weeks at 71°C) Tg values and % char yield at 580°C for these systems are exhibited below.

Thermal and Thermomechanical Properties of Cured Epikote 828/MY720 (1:1 by wt.) Mixtures

Curative in Formulation: (% of Stoichiometry)	Tg dry (a) °C	Tg Wet/°C	%Char Yield at 580°C N ₂	%Char Yield at 580°C Air
Examples of invention				
50% DADS/50% Cpd. I	209	153	37	44
50% DADS/50% Cpd. II	220	152	39	43
50% DADS/50% Cpd. VII	236	167	37	37
100% Compound I(b)	227(c)			46(d)
Comparative example				
100% DADS	221	159	30	25

(a) - all Tg values (modulus loss, E', not tan delta) based on the 3 point-bending DMA method

(b) - solvent mixed system, all the rest are hot melt

(c) - Tg value for fibre reinforced system using dual cantilever method

(d) - char yield for non fibre reinforced system

The glass transition temperatures for all systems, as measured by modulus loss E'' , was high ($>200^{\circ}\text{C}$). The T_g values as indicated by the tan delta peak was $>20^{\circ}\text{C}$ higher in all cases. As expected the wet T_g values are less than for the corresponding dry T_g formulation - nevertheless they remain in the $150\text{-}160^{\circ}\text{C}$ area and as such could find potential application in not only interior furnishing applications but also in structural areas. The char yield under N_2 and air gives an indication of the stability of the char produced upon thermal degradation, and may also relate to the amount of stable char remaining after combustion. Clearly the phosphazene containing samples are distinctly superior to the sample containing only DADS.

These measurements also confirm that Compound VII, an example of a nitrogen linked spirocyclic phosphazene, is an effective curative for epoxy resins. It produces a cured resin with high wet and dry T_g values and improved char yield, compared to a formulation based on DADS as the sole curative.

Example 9:

Flammability Properties of Cured Epoxy Systems Containing Compound I

The epoxy resin system chosen for this study was Epikote 828/Araldite MY 9512 (1:1 by weight). In all cases a stoichiometric quantity of amine curative was employed - either as one component or as unequal quantities of two components. The epoxy resins were mixed and cured according to the general method detailed at the beginning of the Experimental Examples.

Samples thus produced were then cut to 100x100x3mm for use as cone calorimetry test-pieces. Four or five test-pieces were typically used per example formulation. Flammability data based on cone calorimetry testing are shown for the following systems:

- (A) 100% of DADS in 1:1 Epikote 828/MY 9512 (comparative example)
- (B) 90% of DADS/10% Cpd. I in 1:1 Epikote 828/MY 9512 (invention)
- (C) 80% of DADS/20% Cpd. I in 1:1 Epikote 828/MY 9512 (invention)
- (D) 70% of DADS/30% Cpd. I in 1:1 Epikote 828/MY 9512 (invention)

Averaged Flammability Data for Untoughened Epoxies

Formulation Compound I content (%)	A 0	B 10	C 20	D 30
%P	-	1.04	1.97	2.82
%N	4.01	4.58	5.09	5.55
Av. Peak RHR (kW/m ²)	685	303	191	271
Av. Time to Peak RHR (s)	122	120	183	149
Ignition (s)	69	66	66	66
% Mass Loss	85.6	62.7	46.6	50.4
Av. SEA (smoke) (m ² /kg)	823	880	685	930
Peak SPR (s ⁻¹)	28.4	18.5	9.9	18.8
Av. SPR (s ⁻¹)	5.89	3.96	2.67	3.82
Time to Peak SPR (s)	134	124	128	141
Av. CO (kg/kg)x10 ²	9.67	9.28	8.39	10.2
Peak COPR (kgm ⁻² s ⁻¹)x10 ⁴	22.9	13.2	8.6	16.7
Av. COPR (kgm ⁻² s ⁻¹)x10 ⁴	6.70	4.28	3.13	4.23
Time to Peak COPR (s)	107	118	70	112
Av CO ₂ (kg/kg)	1.32	1.12	1.07	1.07
Av. NO _x (kg/kg)x10 ³	7.0	5.9	5.3	4.1

* Content of Compound I expressed as % of total curative stoichiometry

Heat flux for cone calorimetry experiments was 50 kW/m² in all cases

Abbreviations:-

RHR =rate of heat release

SEA = specific extinction area

SPR = smoke production rate

COPR = CO production rate

The peak RHR (rate of heat release) is clearly best, i.e., lowest since RHR approximates to fire intensity, when the content of Compound I in the formulation is 20% of total curative stoichiometry. The time to reach the peak RHR is also longest for this formulation. All the ignition times are sufficiently close to be practically indistinguishable. Mass loss is least for the same 20% formulation: less than half of the mass is consumed.

Smoke production is least for the 20% level formulation, both in terms of SEA (specific extinction area) and the peak and average SPR (smoke production rates). [The SEA yields a number for the "smoke propensity" of a material by relating the amount of smoke produced, as determined by obscuration of a laser source, to the mass loss rate of the burning material. The $SPR = SEA \times RHR / EHC$ {EHC is the effective heat of combustion, MJ/kg, another cone calorimetric parameter} is often considered to yield a better estimate of the actual "smoke hazard" as it takes into account not only the smoke propensity of a material but also the RHR associated with it].

The amount of CO (the most important and prevalent toxic gas in real fires) is least for the 20% level formulation, both in terms of kg of CO produced per kg of sample burned and the peak and average production rate (COPR) [$COPR = CO \times RHR / EHC$]. Although the time to reach the maximum production rate is relatively rapid for this formulation the peak is sufficiently low to make this no real problem. Carbon dioxide levels are largely uniform. The levels of oxides of nitrogen are very low and decrease as the level of Compound I increases.

Example 10:

DSC Characterisation of Uncured Toughened Epoxy Resin Systems

This example demonstrates that the curative system of this invention is effective for use in a toughened epoxy resin system.

DSC characterisations of the following uncured epoxy systems are presented in the table below:

80% of stoichiometry of DADS/20% of Compound I in 1:1 by weight Epikote 828/MY 9512 with 6-9 % by weight Ultem 1000 added.

The 20/80 stoichiometric ratio of Compound I to DADS was chosen for initial study because it had been found to give optimum performance in similar untoughened epoxy resin formulations (see example 9).

DSC for Toughened Epoxies

Formulation: % Ultem 1000	6	7	8	9
Exotherm Onset Temp. °C	165	168	170	169
Temp. of Max. Exotherm °C	234	240	235	233
Exotherm: ΔH (J/g)	360	351	316	350

The exotherm profiles for all formulations are similar, indicating that over the range studied the toughener loading has little effect, i.e., the Compound I/DADS curative system is effective in these toughened formulations.

Example 11:

DMA and TGA Characterisation of Cured Toughened Epoxy Resin Systems

DMA and TGA characterisation of thermomechanical and thermal properties respectively of cured samples of the above formulations was carried out. The results are shown in the table below:

DMA, TGA of Cured Toughened Epoxies

Formulation: % Ultem 1000	6	7	8	9
DMA: Tg (dry) °C	198	194	193	192
TGA/air: % char at 600°C	42	38	42	43

A slight decrease in glass transition temperature is seen as the loading of toughener is increased. However, similar char yields in air were measured for all samples, indicating that the level of toughener has little effect on this property over this range of incorporation levels. A loading of 7% by weight of Ultem 1000 was chosen for further formulation optimisation.

Example 12:

Flammability Characterisation of Cured Toughened Epoxy Resin Systems

Formulations containing varying ratios of Compound I/DADS amine curatives (0/100% to 30/70% of stoichiometry) in 1:1 by weight Epikote 828/MY 9512 with 7% by weight of Ultem 1000 added were prepared in order to find the optimum incorporation level of Compound I.

Flammability characterisation of cured samples was conducted using both LOI (limiting oxygen index) and cone calorimetry. These results are exhibited in the table below:

Flammability Data for Toughened Epoxies

Compound I content (*)	0	5	10	20a	30
% Phosphorus by wt.	0	0.5	1.0	1.8	2.6
LOI (%)	27	29	28	-	28
Av. Peak RHR (kW/m ²)	585	315	351	386	438
Ignition Time (s)	63	61	60	53	55
% Mass Loss	86	77	72	71	67
Peak SPR (s ⁻¹)	23.2	19.5	21.1	25.3	35.0
Peak COPR (kgm ⁻² s ⁻¹)x10 ⁴	21.3	12.9	22.2	24.9	25.7

* Content of Compound I expressed as % of total curative stoichiometry

a - only two samples evaluated, all others run in triplicate

The LOI is very similar for all these formulations, with the highest value at only 5% incorporation of Compound I. The main conclusions to be derived from the cone calorimeter flammability behaviour are:

1. The peak rate of heat release (RHR), which is one of the main factors determining time to flashover in a real fire situation, is reduced substantially (>40%) by inclusion of only 5% of Compound I.
2. Ignition times are slightly reduced when the Compound I content is increased above 10%.
3. Mass loss decreases as the Compound I content is increased.
4. Smoke accumulation in terms of the peak smoke production rate [SPR] is a minimum at 5% Compound I incorporation.
5. The peak production rate of the toxic gas carbon monoxide (peak COPR) is least for the 5% Compound I formulation.

Overall it would appear that the flammability properties

(ignitability, peak RHR, smoke and CO) are at their optimum when the level of Compound I is ca. 5% of the total amine curative stoichiometry. This corresponds to a surprisingly low phosphorus incorporation level of only 0.5 % by weight.

Example 13:

Thermomechanical Characterisation of Cured Toughened Epoxy Resin Systems

Wet and dry glass transition temperatures were measured by DMA for the formulations from Example 12. The results are shown in the following table:

T_g Data for Toughened Epoxies (DMA)

Onset of Modulus loss			Tan delta peak				
Compound I content (*)	0	20	0	5	10	20	30
T _g (°C dry)	193	192	202	213	208	223	197
T _g (°C wet)	140	145	147	160	160	167	-
Δ T _g (°C dry-wet)	53	47	55	53	48	56	-

* Content of Compound I expressed as % of total curative stoichiometry

For these toughened formulations, the modulus loss by DMA corresponding to the wet T_g is very difficult to detect, and it was only possible to obtain the onset of modulus loss in two cases as shown in the tables. For this reason the tan delta peak values are also quoted.

The results confirm that the incorporation of Compound I in these formulations does not reduce thermomechanical properties (wet or dry T_g), at least for loadings of up to 20% of the total curative stoichiometry.

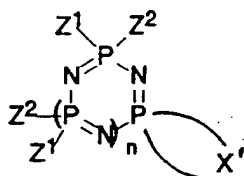
Acknowledgement:

This invention was made as part of work performed by Minnesota 3M Research Ltd, Harlow, UK, in carrying out a project financially supported by the Commission of the European Union DG XII, through the BRITE-EURAM Programme (Project BE 4412, Programme BREU CT 91-0446, Name: "Development of New Materials with Improved Fire Resistance, Reduced Smoke & Toxicity").

CLAIMS

1 A curable composition comprising at least one spirocyclic phosphazene having at least two epoxy curing functionalities and one or more epoxy resins.

2 A curable composition according to Claim 1 wherein said spirocyclic phosphazene has the formula



wherein Z^1 and Z^2 are organic groups or comprise the atoms selected from C, N, O and S required to complete a cyclic structure and

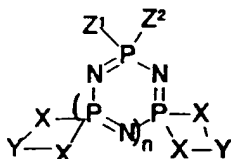
X' represents the atoms selected from C, N, O, S to complete a stable cyclic structure, wherein at least 2 epoxy curing functionalities are present in the molecule either as substituents on one or more of the moieties defined by X' , Z^1 and Z^2 or as integral parts of those moieties.

3 A curable composition according to Claim 1 or 2 wherein at least two of the phosphorus atoms of said spirocyclic phosphazene form part of spiro-linked rings.

4 A curable composition according to any preceding claim wherein said epoxy curing functionalities are selected from amino groups (primary or secondary), amide groups, phenol groups and carboxylic acid groups.

5 A curable composition according to any preceding claim wherein said epoxy curing functionalities comprise amino groups.

6 A curable composition according to any preceding claim wherein said spirocyclic phosphazene has a nucleus of formula 3

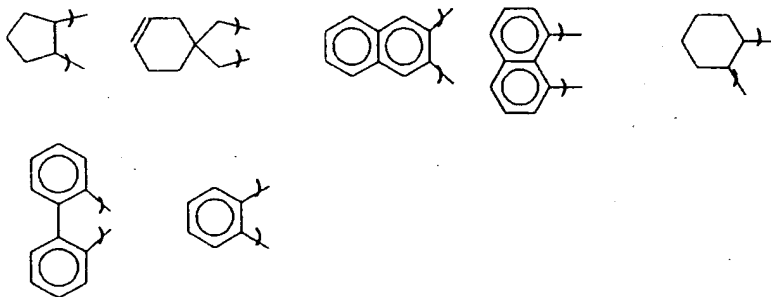


in which n is an integer (preferably 1 or 2);
each X independently represents O, S, or NR where R is H, or alkyl of up to 5 carbon atoms, or aryl of up to 10 carbon atoms;
each Y independently represents the atoms, selected from C, N, O and S, required to complete a stable cyclic structure;
Z¹ and Z² independently represent organic groups, or Z¹ and Z² together represent the atoms, selected from C, N, O and S, required to complete a cyclic structure;
and at least 2 epoxy-curing functionalities are present in the molecule, either as substituents on one or more of the moieties defined by X, Y, Z¹ and Z², or as integral parts of these moieties.

7 A curable composition according to Claim 6 wherein X = O or NH.

8 A curable composition according to Claim 6 or Claim 7 wherein Y is selected from

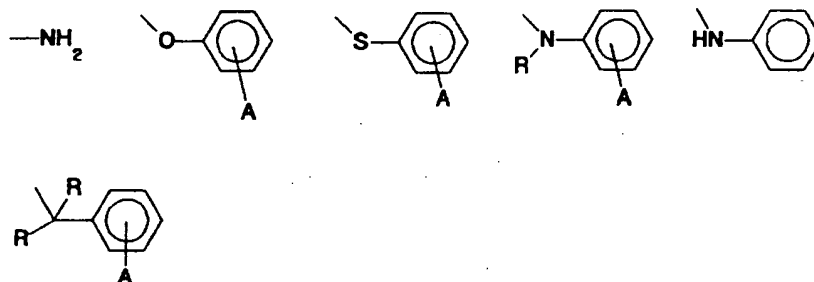
$-(-(CH_2)_{n1}-O-)_{n2}-$, $-(-(CH_2)_{n1}-S-)_{n2}-$, $-(CH_2)_n-$



where -)- indicates the points of attachment to the X groups.

9 A curable composition according to Claim 6, Claim 7 or Claim 8 wherein Z^1 and Z^2 are selected from R^3-X - where X has the same meaning as before and R^3 is H or an alkyl or aryl group substituted with an epoxy curing functionality, or Z^1 and Z^2 together may be represented by the formula $X-Y-X$ where X and Y have the same meaning as before.

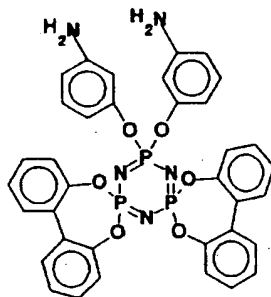
10 A curable composition according to Claim 9 where Z^1 and Z^2 are selected from



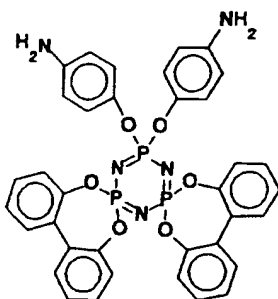
where $A = H, NH_2, NHR, OH$ or SH ; and $R = H$, alkyl or aryl

11 A curable composition according to Claim 10 wherein said spirocyclic phosphazene is selected from

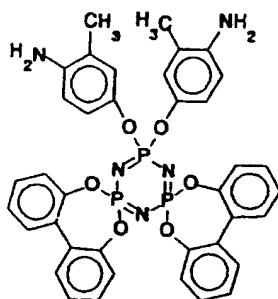
Compound I



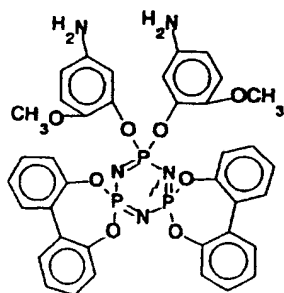
Compound II



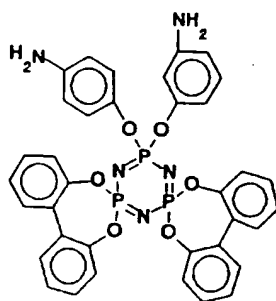
Compound III



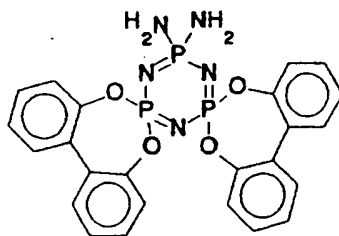
Compound IV



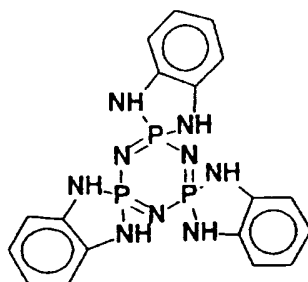
Compound V



Compound VI



Compound VII



12 A curable composition according to any preceding claim further comprising a co-curative for said epoxy resin.

13 A curable composition according to Claim 12 wherein said co-curative is selected from aliphatic and aromatic amines (primary and secondary), anhydrides, organic acids, imidazoles, mercaptans and hydroxy compounds.

14 A curable composition according to Claim 13 wherein said co-curative comprises an aromatic amine.

15 A curable composition according to Claims 14 wherein said co-curative is 4,4'-diaminodiphenylsulphone.

16 A curable composition according to any of Claims 12 to 15 wherein the ratio of phosphazene to co-curative is in the range of 1:99 to 50:50 moles phosphazene to co-curative.

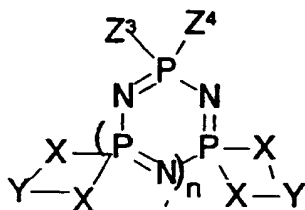
17 A curable composition according to Claim 16 wherein the molar ratio is between 5:95 to 20:80.

18 A curable composition according to any preceding claim wherein said epoxy resin is selected from N,N,N',N'-tetra-glicidyl-4-4-diaminodiphenylmethane, diglycidyl ether of bisphenol A epoxy resin, and mixtures thereof.

19 A curable composition according to any preceding claim wherein the spirocyclic phosphazene curative is present in an amount to provide 0.5 to 2% by weight incorporation of phosphorus into the formulation.

20 A cured composition produced from the curable composition of any preceding claim.

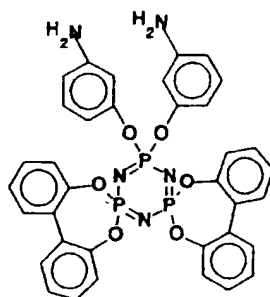
21 A spirocyclic phosphazene having a nucleus of the general formula



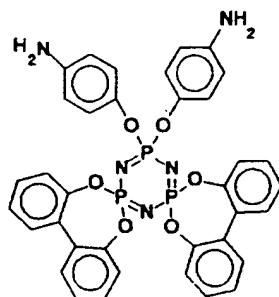
where n is an integer, preferably 1 or 2;
 each X independently represents O, S, or NR where R is H or alkyl of up to 5 carbon atoms, or aryl of up to 10 carbonatoms; each Y independently represents the atoms selected from C, N, O, S required to complete a stable cyclic structure; and Z³ and Z⁴ are independently selected from NHR¹ and -XR² where R¹ is H or aryl and R² is an alkyl or aryl group substituted with an epoxy curing functionality and X has the same meaning as before.

22 A spirocyclic phosphazene according to Claim 21 selected from

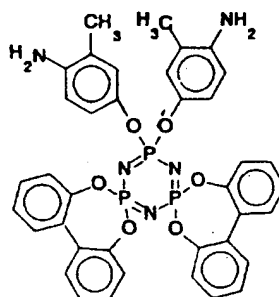
Compound I



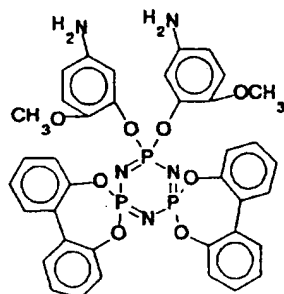
Compound II



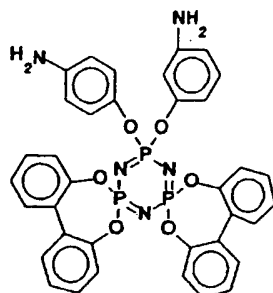
Compound III



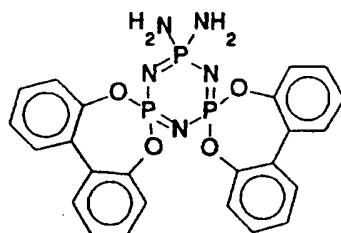
Compound IV



Compound V



Compound VI



- 23 An article comprising the cured composition of Claim 20.
- 24 An article according to Claim 23 further comprising reinforcing fibres or lightweight aramid ^(RTM) honeycomb.
- 25 An article according to Claim 24 in the form of a structural or furnishing component of an aircraft cabin interior.



Application No: GB 9518010.5
Claims searched: 1 to 25

Examiner: Miss M. M. Kelman
Date of search: 21 November 1995

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.N): C2P P2E; C3B BEX

Int Cl (Ed.6): C07F 9/6564, 9/6581, 9/659, 9/6593; C08K 5/5399

Other: ONLINE: CAS-ONLINE, CHEMLIT, PATENTS

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	US 4668589 A KUMAR	1 to 20, 23 to 25
X	Macromolecules Vol. 28(18), 1995, D Kumar and A D Gupta, "Aromatic Cycloliner Phosphazene Polyimides based on a Novel Bis-Spiro-Substituted Cyclotriphosphazene Diamine", pages 6323 to 6329, see especially compounds 5 and 6 on pages 6324, 6325 and 6327	21 and 22

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.